

# Synthesis of Bifunctional Cellulosic Adsorbent by Radiation Induced Graft Polymerization of Glycidyl Methacrylate-co-methacrylic Acids

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**ABSTRACT:** A bifunctional cotton fabric waste bearing  $N^+$   $(CH_2CH_3)_3$  and COOH groups was prepared by radiation induced graft polymerization of glycidyl methacrylate and methacrylic acid using gamma irradiation and subsequent chemical modification of the grafted cotton fabric with triethylamine. Factors affecting the grafting of cotton fabric such as radiation dose and comonomer composition were investigated. The adsorbent was characterized by Fourier transform infrared spectroscopy and scanning electron microscope. Functional groups were tested for its potential application in the removal of cobalt ( $Co^{2+}$ ) and nitrate

( $NO_3^-$ ) from aqueous solutions. Batch experiments were performed to evaluate the adsorption efficiency of the modified grafted cellulose (MGC) towards the cation and the anion. The adsorption capacity for  $Co^{2+}$  at pH 3 and pH 5 was 36.0 and 38.5 mg/g, respectively, whereas that of nitrate was 11 mg/g at pH 4.5. The adsorption process of  $Co^{2+}$  and nitrate obeys both Freundlich and Langmuir isotherm models and followed Pseudosecond order kinetics. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** cellulose; radiation; grafting; adsorption

## INTRODUCTION

Many industries such as painting, textile, metal coating, pulp and paper, printing, rubber, and leather use heavy metal in their process. Heavy metals are very toxic elements and are not biodegradable like many organic pollutants. The discharge of wastewater with heavy metals into natural water from these industries causes detrimental effects on human health and environment. Therefore heavy metals have to be removed from wastewater. Many processes have been used for the removal of heavy metals from industrial effluents such as chemical precipitation, membrane filtration, ion exchange, and adsorption. Adsorption process is one of most frequently used methods to remove heavy metals from aqueous solutions, as it offers the most economical and effective treatment. There are many types of adsorbents that have been studied for the adsorption of ions from aqueous solutions including activated carbon,<sup>1</sup> chitosan,<sup>2</sup> peat,<sup>3</sup> cellulose,<sup>4</sup> chelating fibers,<sup>5</sup> and chelating resins.<sup>6</sup> Removal of heavy metal ions by functionalized polymer has become an important option in the integrated approach to wastewater

treatment. Previous works highlighted the ability of cellulose to adsorb metal ions.<sup>7,8</sup> However, this material itself has low adsorption capacity as well as poor physical stability. Graft copolymerization is one of the most promising methods for the modification of polymeric substances. Various cellulose derivatives have been used as ion exchangers or chelate resins because of their high chemical and mechanical stability and hydrophilic character.<sup>9–13</sup> Among different innovative techniques used for the production of sorption-active materials, the application of economical and ecologically clean radiation technologies is now under attention of research.<sup>14,15</sup> In particular, the utilization of radiation-induced graft polymerization technique allows to introduce inert polymeric matrix the chains of a monomer with a desirable functional groups, or to graft the chains of a precursor-monomer, which can be subsequently modified.<sup>16–18</sup> The substitution of amine functional groups on the backbone of the cellulosic materials increases the number and changes the nature of reaction sites capable of adsorbing certain metal ions in the solution.

In this work, the ability of a bifunctional cellulose-based anion exchanger, amine-modified poly (GMA-co-MAA)-grafted-cellulose having  $N^+$   $(CH_2CH_3)_3$  and COOH groups, to remove cobalt and nitrate from aqueous solutions was investigated under various conditions including contact time, solution pH and initial  $Co^{2+}$  and  $NO_3^-$  concentrations, where

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GMA is glycidyl methacrylate and MAA is methacrylic acid. Attention was also given to evaluate the kinetic constants and mechanism of ion removal.

## EXPERIMENTAL

### Materials

Cobalt  $\text{CO}^{2+}$  was used as cobalt chloride hexahydrate  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . It is red crystal and easily soluble in water. Nitrate was used as aluminum nitrate  $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ . They were supplied by Al-Gomhoria (Cairo, Egypt). GMA and triethylamine were supplied by Merck (Germany). All chemical reagents were used without purification.

Sample of cellulosic fabrics was supplied by Miser (El-Mahala, Egypt) for spinning and weaving. The cotton fabrics used in this study are considered waste fabric pieces from different tailoring process, being well-scoured, and bleached plain weave cotton fabric.

### Graft polymerization

To a known weight of cotton fabric waste, placed in a round bottomed flask, an appropriate amount of GMA and MAA, of different compositions (20 : 80, 30 : 70, 40 : 60, 50 : 50, 60 : 40, 70 : 30, and 80 : 20) dissolved in methanol/water mixture (60 : 40 v/v) and 50% solvent concentration was added. The polymerization reaction was allowed to proceed using  $^{60}\text{Co}$  gamma source with different irradiation doses. The resulting grafted cotton fabric waste was washed thoroughly with ethanol and then with hot distilled water to dissolve any homopolymer that may be attached to the surface of cotton fabric. The grafted sample was then dried at  $60^\circ\text{C}$  to constant weight. The grafting percent was determined by the percentage increase in weight according to the following relationship:

$$\% \text{ Grafting} = \frac{W_g - W_o}{W_o} X$$

Where  $W_o$  and  $W_g$  represent the initial and grafted weight of fabric waste, respectively.

### Conversion of epoxy group to triethylamine

Poly (GMA-co-MAA) was chemically modified using excess of triethylamine as follows: triethylamine (3.5 g 0.1 mg) was dissolved in dimethylformamide (100 mL) and added to grafted cotton fabric (5 g, 0.021 mol epoxide). The mixture was heated at  $100^\circ\text{C}$  for 72 h. The chemically modified cotton fabric was then collected, washed with ethanol, water, and finally with acetone. After exhaustive extraction with acetone, the chemically modified cotton fabric was dried at  $60^\circ\text{C}$  overnight.

### Adsorption experiments

To determine the adsorption isotherm, a known mass (1 g) of the adsorbent, that is, chemically modified cellulose-poly (GMA-co-MAA) was immersed in a series of different initial concentration (100, 200, 300, 400, and 500 mg/L) at pH 3 and pH 5 in case of cobalt and (50, 100, 150, 200, and 250 mg/L) at pH 4.5 in case of nitrate. The adsorbent and pollutant<sup>s</sup> solution (100 mL) were placed in 125 mL glass-stoppered flask and then left for 24 h at room temperature ( $25^\circ\text{C}$ ). The concentration of the resultant solution was then determined by atomic absorption in case of  $\text{Co}^{2+}$  and ion chromatography in case of nitrate. The concentration of  $\text{Co}^{2+}$  and nitrate at equilibrium  $q_e$ , experimental, (mg/g), was calculated by Eq. (1)

$$q_e = \frac{(C_o - C_e)v}{w} \quad (1)$$

Where  $C_o$  and  $C_e$  (mg/L) are the liquid phase concentration of  $\text{Co}^{2+}$  and nitrate at initial and equilibrium state, respectively,  $v$  is the volume of the solution (L) and  $w$  is the mass of dry adsorbent used (g).

## INSTRUMENTS AND TECHNIQUES

### Atomic absorption

The concentration of heavy metal ion was determined by atomic absorption instrument (Unicam Model Solar 929).

### Ion chromatography

The concentration of nitrate was determined by ion chromatography instrument.

### Scanning electron microscope (SEM)

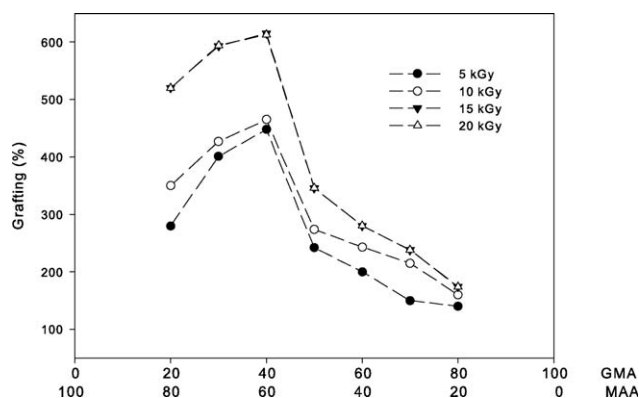
The morphology of original grafted and modified cotton fabric was measured by scanning electron microscope JEol SEM-25 (Japan).

### Ftir spectroscopy

Analysis by infrared spectroscopy was carried out using Perkin-Elmer 16 PC Fourier- Transform infrared spectroscopy (FTIR).

### Gamma radiation source

Irradiation of samples was carried out by using  $^{60}\text{Co}$  gamma source installed at the National Center for Radiation Research and Technology (NCRRT), Egypt with a dose rate of 1.28 Gy/s, with doses ranged from (5–20 kGy).

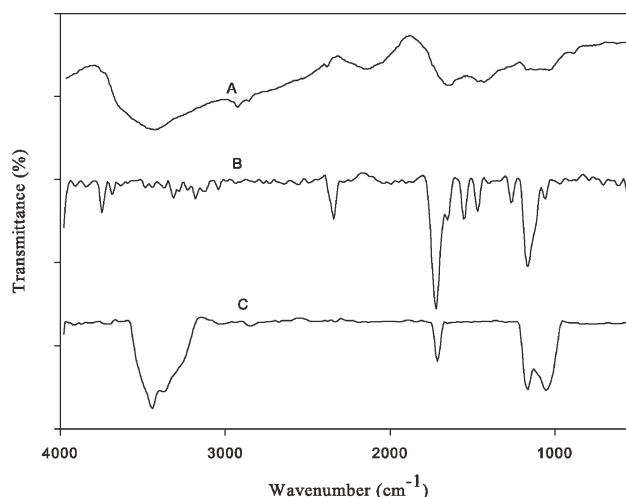


**Figure 1** Relationship between monomer composition (%) and grafting (%) at different irradiation doses (kGy).

## RESULTS AND DISCUSSION

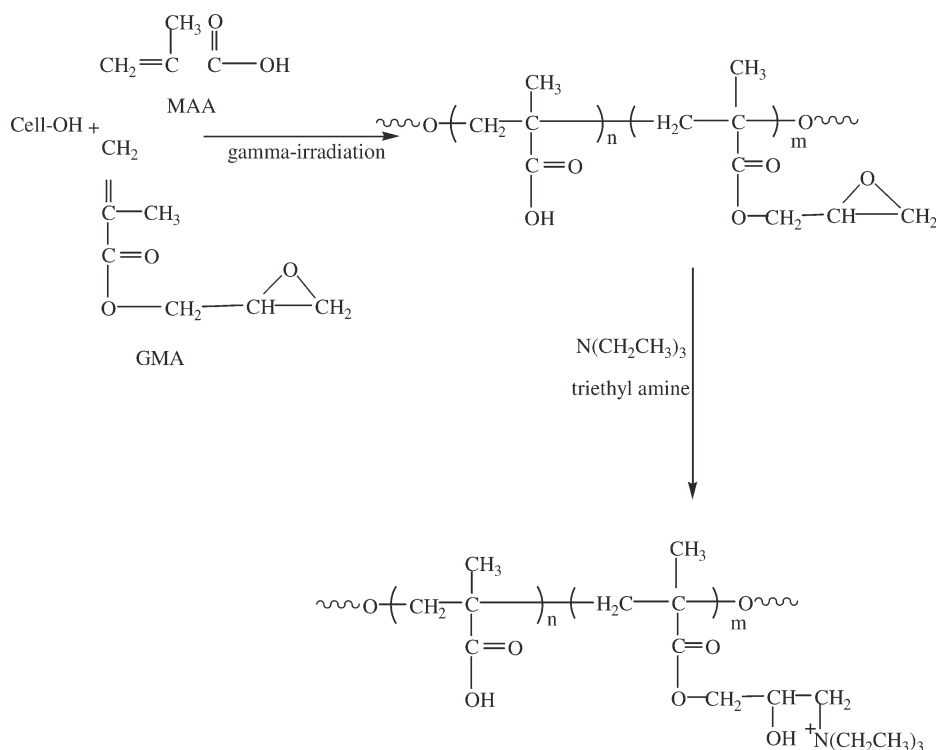
### Effect of comonomer composition on the grafting parentage

The grafting of MAA/GMA binary monomer mixtures of various compositions onto cotton fabric waste is investigated at comonomer concentration 50% (wt %) in methanol/water mixture (60 : 40 v/v) as a solvent. Figure 1 shows the effect of comonomer composition on the degree of grafting of MAA/GMA binary mixture onto cotton fabric waste. It is obvious that, for MAA/GMA binary mixture, the grafting % increases with increasing the content of MAA in comonomer feed solution to reach maximum value at

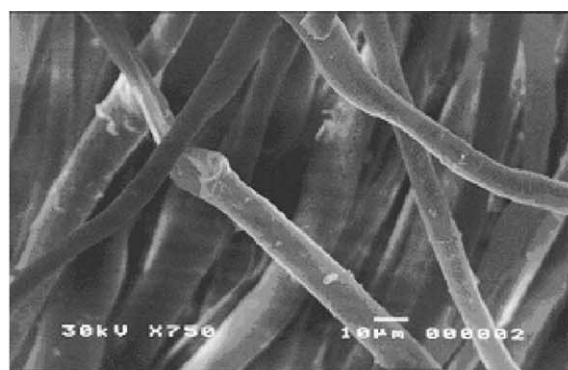


**Figure 2** Shows the FTIR spectra of (a) original cotton fabric, (b) grafted with (MAA-co-GMA) and (c) chemically treated grafted cotton fabric with triethylamine (grafting % 427).

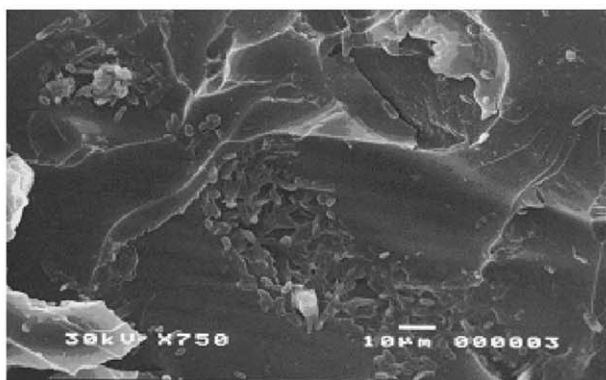
60/40 wt % of MAA/GMA comonomer composition, whereas the degree of grafting decreases with increase GMA content and falls down at 20/80 wt % of MAA/GMA comonomer composition. This may be due to the fact that the reactivity of MAA is higher than that of GMA, in addition at high GMA content a dense-gelled homopolymer is formed, which restrict the diffusion of the comonomer into the interior part of the polymer to initiate new grafting site<sup>19</sup> and thus, retard the grafting process.



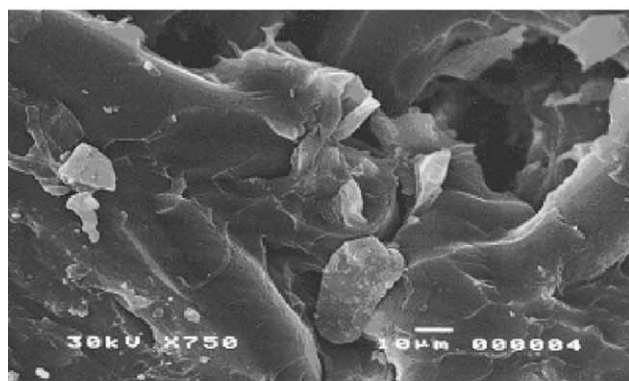
**Scheme 1** The proposed mechanism of grafting of MAA/GMA binary monomers onto cotton cellulosic fiber and the ring opening of the epoxy group to introduce the amine group.



(a)



(b)

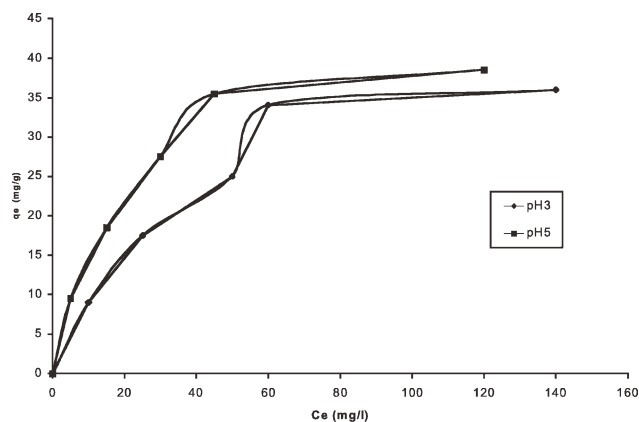


(c)

**Figure 3** SEM of (a) original cotton fabric, (b) grafted with poly (MAA-co-GMA), and (c) chemically treated grafted cotton fabric with triethylamine.

#### Effect of irradiation dose on the grafting parentage

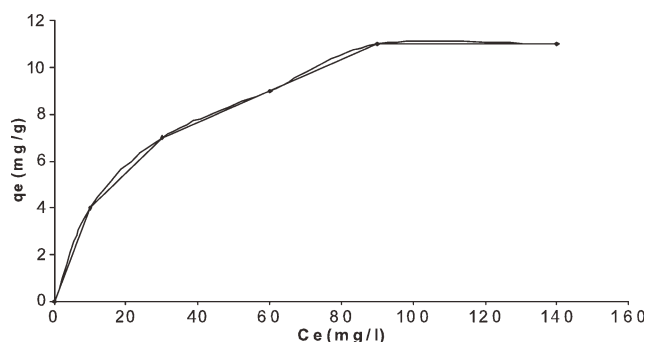
As this graft copolymerization is initiated by the use of  $^{60}\text{Co}$  gamma irradiation in which the process is mainly free radical mechanism. Therefore, the grafting is governed by the concentration of free radicals formed in both the polymer substrate and the comonomer solution. The influence of the irradiation dose on the grafting % of MAA/GMA onto cotton fabric waste was investigated and shown in Figure 1. It is obvious that the grafting % increases with increasing



**Figure 4** Equilibrium adsorption isotherm of Co (II) onto chemically modified grafted cotton fabric waste at different pH values.

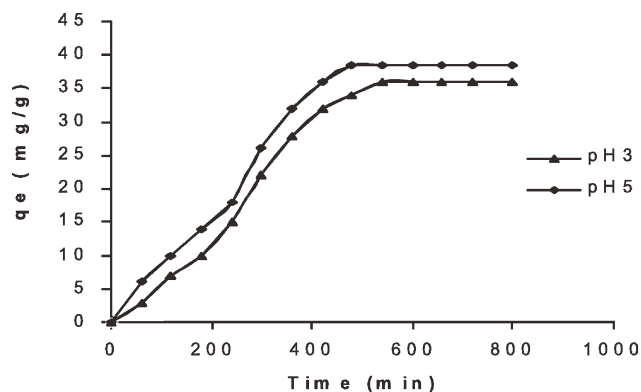
irradiation dose for the binary mixture MAA/GMA from 5 to 15 kGy, then, at high irradiation dose (20 kGy) the degree of grafting tends to level off. It can be assumed that the increase in the irradiation dose resulted in an increase in the concentration of free radicals formed in the trunk polymer as well as in the comonomer binary system. At higher dose, no more active sites are formed and the constant concentration of the free radicals also gives curvature relationship for grafting % with dose. This is due to combination of some radicals without initiating new grafting sites.<sup>20,21</sup> Also the leveling off could be traced back to the fact that, at high levels of grafting the reaction becomes a diffusion controlled process.<sup>22</sup>

From the previous study,<sup>11,13</sup> it was found that the cotton fabric waste, when irradiated with a monomer composition of 70/30 (MAA/GMA) and irradiation dose of 10 kGy, showed a degree of grafting of 427% without any change in the fabric properties. Therefore, it will be applied for the removal of different metal ions from their solutions after chemical modification with triethylamine.



**Figure 5** Equilibrium adsorption isotherm of nitrate onto chemically modified grafted cotton fabric waste at pH 4.5.





**Figure 6** Effect of time on the adsorption capacity of Co (II) onto chemically modified grafted cotton fabric waste at 30°C at different pH values.

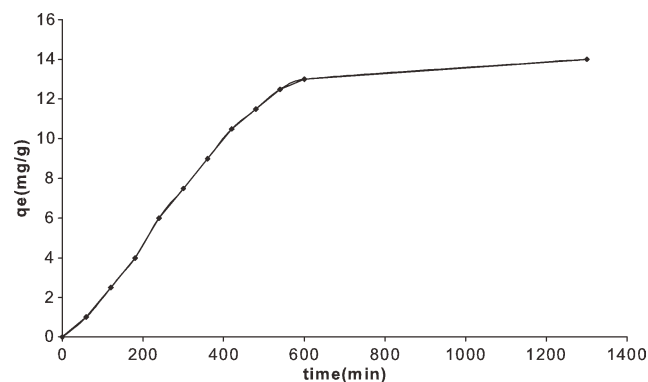
## Characterization

### Infrared spectroscopy

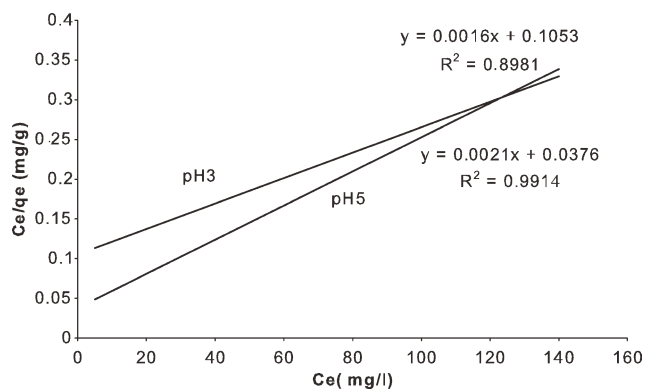
Figure 2 shows the FTIR spectrum of original cotton fabric [Fig. 2(a)], grafted with (MAA-co-GMA) [Fig. 2(b)] and chemically treated grafted cotton fabric with triethylamine [Fig. 2(c)]. The FTIR spectrum of the grafted cotton fabric [Fig. 2(b)] shows the adsorption band at  $1725\text{ cm}^{-1}$ , arising from C=O vibration of carbonyl group, characteristic for (MAA) as well as three bands at  $1264$ ,  $950\text{--}815$ , and  $715\text{ cm}^{-1}$  attributed to epoxy ring. This confirms the grafting of GMA and MAA onto cotton fabric. After amination of grafted cotton fabric with triethylamine the characteristic bands of epoxy ring disappeared and a new bands appeared at  $3420$  and  $1000\text{--}1350\text{ cm}^{-1}$  characteristic for N-H stretching of amino groups and C-N, respectively, as shown in Scheme 1.

### Scanning electron microscope (SEM)

Figure 3 shows the scanning electron microscope of original cotton fabric [Fig. 3(a)], grafted with poly (MAA-co-GMA) [Fig. 3(b)] and chemically treated



**Figure 7** Effect of time on the adsorption capacity of nitrate onto chemically modified grafted cotton fabric waste at 30°C.



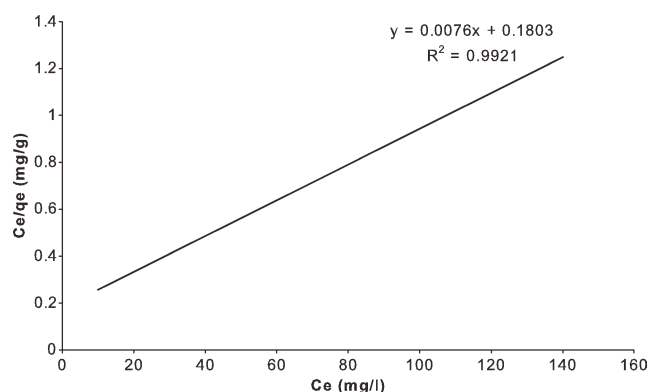
**Figure 8** Langmuir adsorption plot of Co (II) onto chemically modified grafted cotton fabric waste at different pH values.

grafted cotton fabric with triethylamine [Fig. 3(c)] to evaluate its surface morphology. According to our knowledge the image of cellulose exhibits distinct flake and lumpish structure because of the strong intramolecular hydrogen bonds. However, the porous SEM image of grafted and chemically treated grafted cotton fabric Figure 3 indicated that the adding of monomeric units into cellulose units hampered the formation of the intramolecular hydrogen bonds. This kind of loose and porous structures was favorable for producing good sorption properties.<sup>23</sup>

## ADSORPTION OF $\text{CO}^{2+}$ ONTO MODIFIED GRAFTED COTTON FABRIC

### Effect of ion concentration

The effect of initial ion concentration ( $\text{Co}^{2+}$ ) on the adsorption efficiency by modified grafted cotton fabric was systematically investigated by varying the initial concentration between 100 and 500 mg/L. Figure 4 shows the adsorbed amount of  $\text{Co}^{2+}$  ions as a function of initial concentration at pH 3 and 5. It is clear from the figure that as the concentration of the ions increased the adsorption increased rapidly, then



**Figure 9** Langmuir adsorption plot of nitrate onto chemically modified grafted cotton fabric waste at pH 4.5.

**TABLE I**  
Langmuir Constants and Correlation Coefficient by Triethylamine Incorporated Poly (MAA-co-GMA) Cotton Fabric Waste for Adsorption of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$

	$a_L$ (l/g)	$k_L$ (l/g)	$Q_{\max}$ (mg/g)	$b$	$R^2$
$\text{Co}^{2+}$ (pH = 3)	0.015	9.557	500	0.015	0.999
$\text{Co}^{2+}$ (pH = 5)	0.0565	26.47	500	0.0565	1.0
$\text{NO}_3^-$ (pH = 4.5)	0.042	5.55	250	0.042	1.0

leveled off for  $\text{Co}^{2+}$ . The maximum adsorption capacity for  $\text{Co}^{2+}$  was achieved at 36.5 and 38 mg/g at pH 3 and 5, respectively. The nature of the polymer and sorption rate is generally complicated by many possible interactions on the surface, commonly the electrostatic interaction, surface complexation, and ion exchange mechanisms. In particular, the metal uptake will eventually undergo bond complex formation between metals and carboxyl groups present in the polymer.<sup>24</sup> Many previous works used grafted cellulose for removal of cations and anions from waste water [10, 11, 13, and 25]. But those studies were at low initial concentration (10 mg/L) of Fe, Cr<sup>25</sup> and nitrate.<sup>11</sup> The adsorption efficiency was lower to some extent compared with the results obtained in this study.

### Effect of the pH

The adsorption behavior of the metal ion ( $\text{Co}^{2+}$ ) on the modified grafted cotton fabric at pH 3 and 5 at fixed treatment time (24 h.) was examined and the results are shown in Figure 4. It is clear that increasing pH value, that is, by decreasing the hydrogen ion concentration in the solution, is accompanied by a detectable increase in the adsorption for the heavy metal ion under investigation. This may be attributed to the hydrolysis of the metal ions at higher pH values.<sup>26</sup>

### Adsorption of nitrate

Figure 5 shows the adsorption isotherm of nitrate anion onto modified grafted cotton fabric at initial concentration between 50–250 mg/L at pH 4.5.<sup>27</sup> It can be seen that the adsorption capacity of modified cotton fabric increased with increasing initial concentration of nitrate ions in the medium. The maximum adsorption capacity was 11 mg/g. The anion

**TABLE II**  
Effect of Separation Factor  $R_L$  on Isotherm Shape

$R_L$ value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

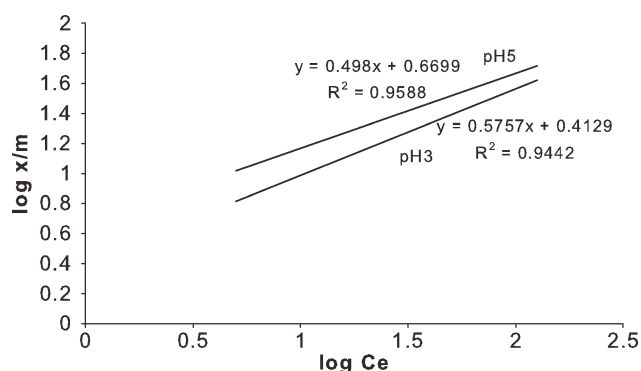
**TABLE III**  
 $R_L$  Values Based on Langmuir Equation for  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  onto Modified Grafted Cotton Fabric Waste

$\text{Co}^{2+}$ (pH 3)		$\text{Co}^{2+}$ (pH 5)		$\text{NO}_3^-$ (pH 4.5)	
Initial concentration (mg/l)	$R_L$ value	Initial concentration (mg/l)	$R_L$ value	Initial concentration (mg/l)	$R_L$ value
100	0.4	100	0.15	50	0.32
200	0.25	200	0.08	100	0.19
300	0.18	300	0.05	150	0.13
400	0.14	400	0.04	200	0.10
500	0.11	500	0.03	250	0.08

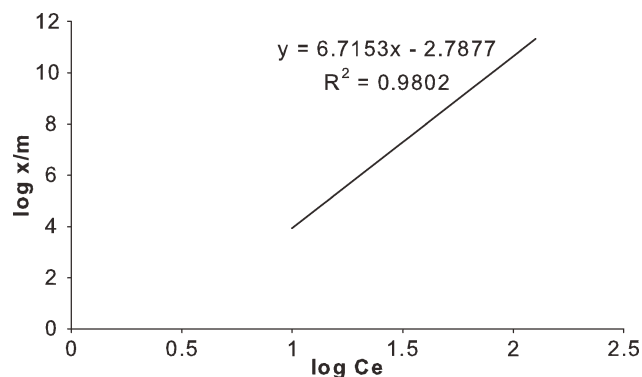
adsorption depends on the protonation or unprotonation of functional groups on the surface of the adsorbent. At acidic pH, the amino groups of modified grafted cotton fabric are positively charged, which leads to electrostatic attraction for the negatively charged nitrate ions. In other words, at lower pH the protonation of the binding sites of the sorbent resulting from a high concentration of protons causes an increase of the binding of nitrate ions.<sup>28</sup> In this adsorption system, the binding of nitrate is achieved by ion chelating property of the amine groups of modified grafted cotton fabric.

### Effect of time

Figures 6 and 7 show the effect of time on the adsorption capacity of  $\text{Co}^{2+}$  (at pH 3 and 5) and nitrate ions at pH 4.5 onto modified grafted cotton fabric at fixed ion concentration 500 mg/L in case of  $\text{Co}^{2+}$  and 250 mg/L in case of nitrate at 30°C. It is clear from the figures that the amount of ions adsorbed increases with the increasing of time and reached the equilibrium after 460 min. The adsorption curve is single and continuous leading to saturation, which indicate the possibility of formation of monolayer coverage of metal ions on modified grafted cotton fabric surface.



**Figure 10** Freundlich adsorption plot of Co (II) onto chemically modified grafted cotton fabric waste at different pH values.



**Figure 11** Freundlich adsorption plot of Nitrate onto chemically modified grafted cotton fabric waste at pH 4.5.

### Adsorption isotherms

The adsorption isotherm was obtained from batch experiments and two theoretical isotherm models were used to fit the experimental data: Langmuir and Freundlich. The Langmuir isotherm model assumes monolayer adsorption with equal energy and enthalpy for all adsorption sites and takes the form below<sup>29–31</sup>:

$$q_e = \frac{k_L C_e}{1 + a_L C_e} \quad (2)$$

The Langmuir equation can be determined from the linear form from Eq. (2), represented by Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{k_L} + \frac{a_L}{k_L} C_e \quad (3)$$

Where,  $C_e$  is the equilibrium concentration of  $\text{Co}^{2+}$  and nitrate ions used (mg/L).  $q_e$  is the amount adsorbed (mg/g). The constants  $k_L$  and  $a_L$  are the Langmuir constant (L/g) and Langmuir isotherm constant (L/mg), respectively. The ratio of  $k_L/a_L$  represents the maximum adsorption capacity ( $Q_{\max}$ ). Therefore, the plots of  $(C_e/q_e)$  versus  $C_e$  give a straight line as shown in Figure 8 for  $\text{Co}^{2+}$  (at pH 3 and 5) and Figure 9 for nitrate ions (at pH 4.5) with slope of  $a_L/k_L$  and intercept of  $1/k_L$ . The Langmuir constants of adsorption of  $\text{Co}^{2+}$  and nitrate ions onto modified grafted cotton fabric and  $R^2$  value are listed in Table I. From Figure 8, it can be seen that

**TABLE IV**  
Freundlich Constants and Correlation Coefficient by Triethylamine Incorporated Poly (MAA-co-GMA) Cotton Fabric Waste for Adsorption of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$

	$k_f$	$n$	$R^2$
$\text{Co}^{2+}$ (pH 3)	2.75	1.8	0.92252
$\text{Co}^{2+}$ (pH 5)	2.95	1.79	0.9284
$\text{NO}_3^-$ (pH 4.5)	1.68	2.49	0.96571

the correlation coefficient ( $R^2$ ) was 0.999 and 1.0 in case of  $\text{Co}^{2+}$  at pH 3 and 5, respectively, and 1.0 in case of nitrate. The essential feature of Langmuir model can be expressed in terms of dimensionless separation factor<sup>32</sup> or equilibrium parameter  $R_L$  (Tables II and III) given by the relation:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The Freundlich isotherm model is based on the assumption of adsorption on heterogeneous surfaces and possibly in multilayer adsorption and is usually given as<sup>33,34</sup>:

$$q_e = k_f C_e^{1/n} \quad (5)$$

Where  $k_f$  is the Freundlich constant depicting adsorption capacity,  $1/n$  is a constant indicating adsorption capacity,  $C_e$  (mg/L) and  $q_e$  (mg/g) have the same definition as before. In general, as the  $k_f$  value the adsorption capacity increases. Values of  $n$  show favorable adsorption on adsorbent if  $n$  values are between 1 and 10.  $k_f$  and  $n$  are determined from the liner plot of  $\log q_e$  versus  $\log C_e$ . Freundlich plot of metal ions at pH 3 and 5 for  $\text{Co}^{2+}$  and pH 4.5 in case of nitrate onto modified cotton fabric is shown in Figures 10 and 11. The values of Freundlich constants are listed in Table IV. It is clear from this table that the values of  $n$  for  $\text{Co}^{2+}$  and nitrate ions ( $0 < n < 10$ ) indicating that the adsorption of this pollutants onto the prepared adsorbent is favorable. The correlation coefficient  $R^2$  value was 0.9225, 0.9284 for  $\text{Co}^{2+}$  at pH 3 and 5 and 0.9657 for nitrate indicating that the adsorption of  $\text{Co}^{2+}$  and nitrate is fitted well with Freundlich isotherm.

**TABLE V**  
Parameters of Pseudo-First Order Adsorption Rate Constant for  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  onto Modified Grafted Cotton Fabric

	Initial concentration	$q_e$ (Exp.) (mg/g)	$q_e$ (calc.) (mg/g)	Adsorption rate constant $k_1$ (g/mg/min)	$R^2$
$\text{Co}^{2+}$ (pH 3)	500	36	1.4269	-54.598	0.6404
$\text{Co}^{2+}$ (pH 5)	500	38.5	1.4276	$-7.48 \times 10^{-4}$	0.7405
$\text{NO}_3^-$ (pH 4.5)	250	11	1.4269	-3333.3	0.7404

TABLE VI  
Parameters of Pseudo-Second Order Adsorption Rate Constant for  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  onto Modified Grafted Cotton Fabric

	Initial concentration	$q_e$ (Exp) (mg/g)	$q_e$ (calc.) (mg/g)	Adsorption rate constant $k_2$ (g/mg/min)	$R^2$
$\text{Co}^{2+}$ (pH 3)	500	36	17.8	$2.3 \times 10^{-3}$	0.8674
$\text{Co}^{2+}$ (pH 5)	500	38.5	20	$1.5 \times 10^{-4}$	0.9485
$\text{NO}_3^-$ (pH 4.5)	250	11	30.3	0.015	0.8907

### Adsorption kinetics

Adsorption kinetic data are often analyzed with kinetic models to reveal whether an adsorption process is dominated by a physical or chemical adsorption phenomenon. The most two commonly used kinetic models, that is, the pseudofirst order and pseudosecond order models can be given respectively, in their linearized forms as in eqs. (6) and (7) below<sup>35,36</sup>:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (7)$$

Where  $q_t$  (mg/g) is the adsorption uptake at time  $t$  (min.),  $q_e$  (mg/g) the adsorption capacity at adsorption equilibrium and  $k_1$  ( $\text{min}^{-1}$ ) is the kinetics rate constant for the pseudo-first order model and  $k_2$  (g/mg/min) the kinetic rate constant for the pseudosecond order model.

The plots of  $\ln(q_e - q_t)$  versus  $t$  gave the slope of  $k_1$  and intercept of  $\ln q_e$ . The values of  $k_1$  and correlation coefficient,  $R^2$  obtained from the plots for adsorption of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  onto the modified grafted cotton fabric at 30°C are given in (Table V). The  $R^2$  values were relatively small, which varied from 0.6404 to 0.7405 for  $\text{Co}^{2+}$  initial concentration of 500 mg/L and 0.7404 for  $\text{NO}_3^-$  at initial concentration of 250 mg/L. Besides, the experimental  $q_e$  values did not agree with the calculated values obtained from the linear plots. This shows that the adsorption of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  on the modified grafted cotton fabric is not a first-order reaction.

The linear plot of  $(t/q_t)$  versus  $t$  gave  $1/q_e$  as the slope and  $(1/k_2 q_e^2)$  as the intercept (figure is not included), which is more likely to predict the behavior over the whole range of adsorption. The linear plot of  $t/q_t$  versus  $t$ , shows a good agreement between the experimental and the calculated  $q_e$  values (Table VI). Besides, the correlation coefficient ( $R^2$ ) values for the second-order kinetic model were almost equal to unity for  $\text{Co}^{2+}$  and  $\text{NO}_3^-$ , indicating the applicability of the second-order kinetic model to describe the adsorption process of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  on the modified grafted cotton fabric.<sup>37</sup>

### CONCLUSIONS

A bifunctional cotton fabric waste was synthesized by radiation induced graft polymerization of poly (MAA-co-GMA) onto the cotton fabric and subsequent chemical modification with triethylamine. The prepared adsorbent was successfully applied for removal of  $\text{Co}^{2+}$  and  $\text{NO}_3^-$  from aqueous solutions. The adsorbent exhibit porous structure and affinity towards  $\text{Co}^{2+}$  and  $\text{NO}_3^-$ , through complexation with carboxyl group of MAA and amine group, respectively. The adsorption capacity for  $\text{Co}^{2+}$  at pH 3 and 5 was 36 and 38.5 mg/g, respectively, whereas for  $\text{NO}_3^-$  11 mg/g. The adsorption process follows both Langmuir and Freundlich isotherm models. The adsorption of modified grafted cotton fabric obeys the Pseudo-second order kinetic. The results of this study indicated that the prepared adsorbent is suitable for the development of efficient bifunctional adsorbent for the removal and recovery of metal ions from wastewater.

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